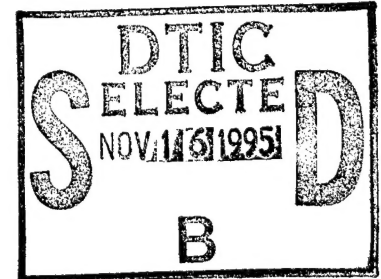




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Environmental
Center**

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FINAL REPORT

Test Plan for Pilot-Scale Demonstration of Red Water Treatment by Wet Air Oxidation and Circulating Bed Combustion



October 1995
Contract No. DACA31-91-D-0074
Task Order No. 0005

Prepared by:

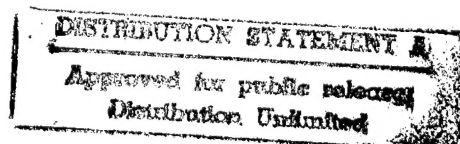
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TEST PLAN

FOR

**PILOT SCALE DEMONSTRATION OF
TREATMENT OF RED WATER BY WET AIR OXIDATION
AND CIRCULATING BED COMBUSTION**

USAEC Contract No. DACA 31-91-D-0074
Task Order No. 5

Prepared by

IT Corporation
Cincinnati, Ohio

October 1995

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Preface

As part of the U.S. Army's ongoing program related to the research and development of red water treatment technologies, the U.S. Army Environmental Center (USAEC) contracted IT Corporation to prepare conceptual designs and plans for pilot-scale demonstrations of two treatment technologies: wet air oxidation (WAO) and circulating bed combustion (CBC). The project objectives included initial development of a Test Plan and Health and Safety Plan for these demonstrations. The Test Plan presented in this document is intended to serve as a guide for the development of a complete Test Plan when the next phase of this program is implemented.

Red water is not currently generated by the U.S. Army or any other part of the U.S. Department of Defense nor has it been generated in the recent past. An accurate and complete database does not exist in regard to the chemical and physical nature of red water. Therefore, it was not possible to complete an accurate analysis of the associated testing and treatment requirements. Additionally, the source of red water for testing and the location where the tests will be conducted (i.e., the host facility) have not been identified. Therefore, waste and site-specific concerns and requirements can not be accurately or completely addressed at this time. Similarly, because this phase of the investigation included completion of conceptual designs only, the assessment of equipment-specific testing procedures is preliminary in nature.

For the reasons presented above, this Test Plan does not, and is not intended to, represent a completed document that is ready for implementation. Out of necessity, this plan is often generic in nature or based on stated assumptions. In the future, when the host facility has been selected and when red water is available for pilot-scale testing, this plan will be available for review, revision, and expansion to reflect specific conditions and requirements associated with the host site, the actual equipment, and the specific waste. Because of the unique and largely undocumented nature of red water, once a source has been identified a critical initial objective will be characterization of its physical and chemical nature and the associated treatment requirements.

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1.0 Introduction

The production of trinitrotoluene (TNT), the major component of most of the Department of Defense's explosives, generates a wastewater stream called red water. Because of its reactivity, red water has been listed as a hazardous waste (K047) by the U.S. Environmental Protection Agency (U.S. EPA) under Subtitle C, Part 265 of the Resource Conservation and Recovery Act (RCRA). Four Army Ammunition Plants (AAPs) -- Radford, Joliet, Newport and Volunteer -- are equipped with production facilities necessary for the manufacture of TNT. However, the TNT production facilities at these AAPs are currently idle and in mothballed status. None of these facilities has produced TNT during recent years because the military's peace-time requirement is too small to justify the high cost of operation. Additionally, none of the AAPs currently has the capability to treat or dispose of red water.

Demonstration of an acceptable waste treatment technology is an important aspect in increasing the readiness of these facilities to mobilize TNT production capability. It is anticipated that at a future time, the U.S. Army Environmental Center (USAEC) will conduct a demonstration to evaluate potential methods for treating red water. Previously, a comparative evaluation of 30 potential technologies for the treatment of red water was completed by the USAEC. Two technologies -- circulating bed combustion (CBC) and wet air oxidation (WAO) -- were concluded to have the potential for successfully treating red water and were sufficiently advanced to warrant pilot-scale testing. These technologies are the subject of this Test Plan.

Because red water is not currently available for testing and because a host facility has not been selected, the first phase of the demonstration is the preparation of conceptual designs and plans. This Test Plan is intended to serve as a starting point for the next phase of activities.

In addition to this Test Plan, other documents prepared for this project include the following:

- Project Report
- Health and Safety Plan
- WAO Conceptual Design Report
- CBC Conceptual Design Report.

Unit operating procedures (UOPs) for equipment operation should be prepared as separate documents prior to testing.

1.1 Objectives

The objective of this Test Plan is to address general testing requirements related to the red water treatment demonstrations. Because the pilot test location (i.e., host facility) has not been determined, this Test Plan is not site-specific. During the next phase of activities, the Test Plan must be revised based on waste, equipment, and site-specific information and changes in field conditions.

The primary objective of the demonstrations is to acquire information necessary for selecting a red water treatment technology for full-scale implementation. The selection will be based on an evaluation of the following:

- Treatment effectiveness
- Reliability
- Estimated life-cycle costs.

Data obtained during the pilot-scale demonstrations will also be useful for scale-up from the pilot-scale to a full-scale application, and identify the design and operational parameters that are important for full-scale implementation.

To fulfill the USAEC's program objectives, tests will be performed to evaluate the effectiveness of the two selected technologies in treating red water. Treatment effectiveness will be evaluated at multiple operating conditions as documented later in this plan. In addition, the consumption of electrical power, natural gas, chemicals, and other utilities and reagents will be monitored during these test runs. These data can be used to estimate requirements of a full-scale system and facilitate calculation of life-cycle costs for such a system so that operating costs can be projected.

1.2 Project Organization

For the purposes of this document, it is assumed that the USAEC will issue a contract to a Task Order Contractor (TOC) to conduct the demonstrations. Further, it is assumed that the TOC will issue two subcontracts for the preparation of final designs and fabrication of pilot-scale WAO and CBC demonstration units. (Such units do not currently exist; hence the need for design and construction.) The assumed general roles and responsibilities of the TOC, its two subcontractors, and the host facility are indicated below:

Task Order Contractor

- Review technologies and recommend selection
- Oversee Final Design preparation
- Define installation support requirements
- Conduct regulatory review
- Assist host facility in revising/obtaining permits
- Prepare Final Design Report
- Procure pilot-scale WAO and CBC units
- Complete and finalize Test Plans and Safety Plans
- Prepare a Site Safety Submission
- Provide on-site coordination and oversight during installation and testing
- Perform industrial hygiene sampling and analysis for chemical and physical hazards
- Perform sampling and analysis to document performance
- Provide photographic documentation
- Prepare a technical project report.

Subcontractor for WAO

- Prepare final design of pilot-scale WAO equipment
- Provide input on Test Plan, Safety Plan, and Site Safety Submission
- Fabricate, ship, install, and operate test equipment for WAO treatment
- Provide input on technical reports.

Subcontractor for CBC

- Prepare final design of pilot-scale CBC equipment
- Provide input on Test Plan, Safety Plan, and Site Safety Submission
- Fabricate, ship, install, and operate test equipment for CBC treatment
- Provide input on technical reports.

Host Facility

- Review and comment on Test Plan and Safety Plan
- Review equipment selection and design
- Conduct hazards review
- Prepare, with TOC input, standard operating procedures
- Provide photographic documentation
- Provide facilities support including utilities and operators
- Provide on-site analytical support
- Review and comment on the technical reports.

These roles have been assumed and defined to ensure that the Test Plan sufficiently addresses the anticipated complexity of the project organization.

1.3 Project Schedule

The schedule for performing the pilot-scale demonstrations has not been determined at this time. It is anticipated that the pilot-scale demonstrations will be completed in the following general sequence:

- Pre-design Activities - approximately 2 months
 - Acquire a source of red water for testing
 - Characterize the red water
 - Identify host facility
- Design and Equipment Acquisition Activities - approximately 6 months
 - Complete pilot-scale systems designs
 - Fabricate equipment
- Pre-test Activities - approximately 1 month
 - Transport and set-up equipment
 - Connect test units to utilities and process points
- Operational Shakedown Tests and Operator Training - approximately 1 month
- Demonstration Tests - approximately 2 months
- Post-test Activities - approximately 1 month
 - Decontaminate, decommission, and demobilize equipment
 - Dispose of test residuals.

A detailed project test schedule should be prepared during the next phase of project activities.

2.0 Waste Stream Characteristics

Red water is the aqueous effluent generated during sellite purification of crude TNT. Red water has a deep red, or sometimes black color, and is a complex mixture. It is anticipated that the characteristics and composition of red water will vary with changes in feed stocks, operating conditions, and handling/storage; however, the degree of variability is as yet unknown. Depending on the TNT production process and the degree of water recycle used, red water generally contains from 15 to over 30 percent solids, has a pH in the range of 7.0 to 9.7, and specific gravity of approximately 1.1. Roughly half of the solids are inorganic salts; the remainder are nitro bodies including mainly sodium sulfonates of trinitrotoluene and an alpha-TNT-sellite complex. TNT is present in trace amounts. Other organic constituents include complex, unidentified dye bodies formed from the photolysis of alpha-TNT by sunlight. Heavy metals present in red water are thought to be a result of acid leaching from the stainless steel reaction vessels and holding tanks (Hercules, 1973).

Red water is a RCRA listed hazardous waste (K047), and is classified as such due to the reactivity of the wastewater. If the solids in the red water are allowed to settle and accumulate, an explosive reaction could occur if initiated by impact, friction, heat or electrostatic discharge (Hercules, 1991). A material safety data sheet (MSDS) does not exist for red water.

The database documenting the chemical, physical, and toxicological characteristics of red water is extremely limited. This is primarily due to the fact that red water has not been generated at Army facilities for a number of years. During the time of generation, the need for detailed characterization did not exist; therefore, an analytical database was not compiled. In addition, during this time, analytical methodology associated with quantitation of the unique compounds present was not well advanced. These factors have resulted in the limited database that exists today. Upon identification and acquisition of a source of red water for testing, a thorough characterization must be conducted to identify hazards. This may involve development or modification of analytical techniques for quantitation of unique compounds in a unique matrix.

The available characteristics of red water are summarized in Tables 2-1 and 2-2. It is anticipated that the composition of red water generated by TNT production may vary significantly (IT Corporation, 1993a and 1993b). This is due in part to the fact that MIL SPEC grade TNT can

be produced over a range of process and operational conditions. Data on the variability of red water is not available at this time. Where available, a range of data is presented.

At this time, it is anticipated that bulk storage, at the test location, of approximately 50,000 gallons of red water will be required. Specific hazards, safety protocols, and regulatory requirements associated with this bulk storage must be assessed based upon the characteristics of the actual red water. Obvious concerns involve secondary containment; control of venting and off gases; temperature and pressure controls; and mixing, control, and handling of solids or precipitates. Specific details and protocols can be defined when the red water has been adequately characterized and when the host facility is determined.

Table 2-1 Available Characteristics of Red Water

<u>Parameter</u>	<u>Unit</u>	<u>Concentration/Range</u>
Chemical Oxygen Demand	mg/L	65,000 - 120,000
Total Solids	% ^a	15 - 30
Specific Gravity	NA	1.1
Nominal Solids Heat Value	BTU/lb	3,200
Suspended Solids	mg/L	32
pH	S.U.	7 - 9.7
Soluble Chloride	mg/L	70
Total Kjeldahl Nitrogen	mg/L	11,129
Nitrate Nitrogen	mg/L	1,739
Nitrite Nitrogen	mg/L	6,788
Ammonia Nitrogen	mg/L	150
Metals	mg/L	
Calcium		39 - 346
Iron		4.9 - 307
Magnesium		25 - 90
Potassium		42
Aluminum		2.1 - 10
Chromium		0.14 - 4.9
Barium		0.22 - 3.0
Copper		2.3
Cadmium		0.7
Silver		0.4
Zinc		6.4

^a Solids analysis provided on Table 2-2

Source: (PEI, 1990)

Table 2-2 Available Data on the Composition of Red Water Solids

<u>Parameter</u>	<u>Weight Percent</u>
Inorganic Salts	
Na ₂ SO ₃ -Na ₂ SO ₄ (sodium sulfite-sodium sulfate)	32.3
NaNO ₂ (sodium nitrite)	11.2
NaNO ₃ (sodium nitrate)	1.5
NaHS-Na ₂ S (sodium sulfide)	may be present
Na ₂ CO ₃ -NaHCO ₃ (sodium bicarbonate-carbonate)	may be present
Subtotal Inorganic Salts	45
Nitrobodies	
Sodium sulfonate of 2,4,5 TNT	22.7
a-TNT-Sellite complex	16.2
Sodium sulfonate of 2,3,4 TNT	9.6
Sodium sulfonate of 2,3,5 TNT	2.0
Sodium sulfonate of 2,3,6 TNT	trace
2,4,6-TNBA (trinitrobenzoic acid) Na salt	1.0
White compound sodium salt ^a	1.0
TNBAL-bisulfite addition compound (trinitrobenzaldehyde)	1.0
TNBOH (trinitrobenzyl alcohol)	1.0
Sodium nitroformate	0.5
3,5-DNBA (dinitrobenzoic acid) Na salt	trace
2,3-DNBA (dinitrobenzoic acid) Na salt	trace
TNB (trinitrobenzene)-Sellite complex	trace
Dissolved 2,4-DNT (dinitrotoluene)	trace
Dissolved a-TNT (trinitrotoluene)	trace
Subtotal Nitrobodies	55

^a "White compound" is believed to be 2,2-dicarboxy-3,3,"5,5"-tetranitroazoxybenzene

Source: (PEI, 1990)

3.0 Probable Discharge Requirements

Under the current Task Order, a document entitled "Waste Management Regulatory Overview for Pilot-scale and Full-scale Treatment of Red Water (K047)" (hereinafter referred to as the "Regulatory Review Report") was prepared and included in the Project Report. The Regulatory Review Report identifies the regulatory issues and anticipated discharge requirements for discharges from red water treatment units. The following subsections summarize the information on regulations pertaining to the residues and emissions generated by the WAO and CBC processes presented in Section 3 of the Regulatory Review Report. This information serves as a basis for determining the objectives of the pilot-scale demonstrations.

3.1 Wastewater

The treatment of red water by WAO results in a liquid effluent that can be sent to:

- A RCRA-permitted treatment, storage, and disposal facility (TSDF)
- A publicly owned treatment works (POTW)
- A National Pollutant Discharge Elimination System (NPDES) permitted discharge point to a body of water.

Each of these three options would require compliance with different treatment standards, analysis of different parameters, and submittal of differing regulatory compliance documentation. Shipment of treated water to a RCRA-permitted TSDF requires the least amount of treatment by the generator, whereas the direct discharge to a receiving body of water requires the greatest degree of treatment. The regulatory considerations for each of the three options are outlined in the following sections.

3.1.1 TSDF Disposal of Treated Red Water

The acceptability of the WAO effluent for treatment by a RCRA-permitted TSDF depends on the limitations of the TSDF in treating waste. Because the red water is a RCRA listed waste, it retains its classification as a RCRA hazardous waste even after treatment, unless formally delisted as discussed in Section 3.1 of the Regulatory Review Report. An incoming waste must be properly characterized according to RCRA (40 CFR 261), Department of Transportation (DOT) (49 CFR), and the operating parameters of the TSDF. The list of required analytical parameters may be modified on the basis of the generator's knowledge of the generation method.

Typical analytical requirements are anticipated to include:

- Explosivity
- Reactivity
- Treatment parameters (e.g., specific gravity; pH; cyanide; sulfide; phenolics; polychlorinated biphenyls; oil and grease; total organic carbon; total organic halogen; total RCRA metals; and toxicity characteristic leaching procedure for metals, volatiles, semivolatiles, pesticides, and herbicides).

Although, for the purposes of this Test Plan, it has been assumed that the WAO effluent will not be sent to an offsite TSDF for disposal, the TSDF requirements are presented to ensure that adequate data are collected.

3.1.2 POTW Disposal of WAO Effluent

Disposal of the treated red water to a POTW subjects it to regulation under Section 402 of the Clean Water Act (CWA), as amended, and, if the tests are conducted in Virginia, to the corresponding Commonwealth of Virginia regulations (VR 680-14-01). Part VII of VR 680-14-01 establishes the legal requirements for state, local government, and industry to implement National Pretreatment Standards for the control of pollutants that pass through or interfere with treatment processes in POTWs or which may contaminate sewage sludge. Section 7.2 of VR 680-14-01 incorporates some federal regulations regarding pretreatment standards. The Virginia regulations incorporate sections of the federal regulations regarding categorical standards, removal credits, POTW pretreatment programs, guidelines for test procedures, variances from pretreatment standards, calculations, by-pass, modification to the POTW's program, and most of the National Categorical Pretreatment Standards. The federal categorical pretreatment standards for explosives manufacturing (40 CFR 457) are not incorporated into VR 680-14-01 by reference. The Virginia State Water Control Board is required by VR 689-14-01 Section 7.2(B) to adopt changes or modifications to the federal regulations or undertake a rulemaking to adopt more stringent control. Whether the Board eventually adopts the federal pretreatment standards for explosive manufacturing or adopts more stringent regulations, the WAO effluent (i.e., treated red water), at a minimum, must meet the limitations established in 40 CFR 457.12 after the application of the best practical control technology currently available.

The federal Effluent Guidelines and Standards for explosives manufacturing are listed in 40 CFR 401 and 40 CFR 457, Subpart A. One of the primary discharge criteria is chemical oxygen demand (COD); the 1-day maximum discharge standard in 40 CFR 457, Subpart A is 7.77 pounds per 1,000 pounds of product. Thus, this standard is based on the rate of TNT production. Information on TNT production from "Evaluation of Six Options for Obtaining Red Water" (IT, April 1993) indicates that a COD standard based on concentration would be a maximum 1-day limit of 11,212 milligrams per liter (mg/L) and a 30-day average of below 3,694 mg/L.

Other discharges prohibited by VR 680-14-01 Section 7.4 include the introduction of pollutants into a POTW that will:

- Pass through or interfere with the operation or performance of the POTW
- Create a fire or explosive hazard in the POTW
- Cause corrosive structural damage to the POTW
- Cause obstruction to the flow in the POTW
- Cause interference with the POTW (including oxygen demand)
- Result in inhibition of biological activity at the POTW due to heat.

The POTW is required by Section 7.4(B) of VR 680-14-01 to develop and enforce specific limits upon the industrial user.

Typical analytical requirements are anticipated to include:

- Explosivity
- Reactivity
- Chemical oxygen demand (COD)
- Biochemical oxygen demand - 5 day (BOD₅)
- Total suspended solids (TSS)
- pH
- Other parameters to be determined by the POTW.

For the purposes of this Test Plan, it is assumed that the WAO effluent may be sent to an offsite POTW or to an onsite wastewater treatment plant that is regulated as a POTW.

3.1.3 Surface Water Discharge of Treated Red Water

The discharge of treated red water to surface water would be subjected to regulation under Section 402 of the CWA. The discharge of treated waste to surface water must be authorized by a NPDES permit per 40 CFR 401, or the Commonwealth of Virginia equivalent (VPDES) per VR 680-14-01, if the facility is in Virginia. Permit limitations are established on a facility-specific

basis to insure compliance with technology-based standards. The discharge of delisted, treated red water to surface water in Virginia would be subject to the Virginia Water Quality Standards (VR 680-21-01).

Typical analytical requirements are anticipated to include:

- Explosivity
- Reactivity
- State water quality criteria (may include metals, SVOCs, VOCs, pesticides, herbicides, ammonia, cyanide, hydrogen sulfide, and polychlorinated biphenyls, etc.).

For the purposes of this Test Plan, it is assumed that the treated water may be discharged directly to a surface water body.

3.2 Air Emissions

3.2.1 Potential Emissions

Potential emissions from the CBC test unit have been estimated, and are presented in Table 1 of the Regulatory Review Report. These estimates are based on the material balance contained in the CBC Conceptual Design Report. Air emissions from the WAO are anticipated to be equivalent or lower.

3.2.2 Overview of Air Regulations

State and federal air pollution control regulations under both the RCRA and Clean Air Act (CAA) programs are potentially applicable to the CBC, and to a lesser degree, to the WAO. The CBC will generate combustion byproducts that will be vented to the atmosphere through a stack after being treated in air pollution control equipment. Because the CBC is technically an incinerator and red water is a RCRA listed waste, the CBC demonstration unit must be permitted as a RCRA hazardous waste incinerator, complying with RCRA air emission criteria. It is anticipated that the pilot-scale CBC would be permitted as a Research, Development, and Demonstration (RD&D) facility.

Because the requirements for a RCRA RD&D permit vary in each application and may not be as stringent as for a non-RD&D permitted facility, pre-permitting conferences should be held with

the regulators to define the extent to which the requirements for a RCRA permitted incinerator will apply. RCRA incinerator regulations include both design standards and operational standards (including emission criteria that must be considered in the design).

The CBC must also comply with state and possibly federal air pollution control regulations. If the unit is sited at a location where it can be considered a stand-alone emission source, the state may require a construction permit before construction can begin. If the unit is considered part of a larger facility (e.g., an AAP), the unit could be subject to a Prevention of Significant Deterioration (PSD) preconstruction permit modification and/or a CAA Title V operating permit.

The WAO will generate less total air emissions (including water vapor, carbon dioxide, nitrogen, oxygen, and other combustion byproducts) than the CBC, but may still require air permits. The reactions taking place in the WAO will generate off-gassing. Treated effluent held in a receiving tank will also off-gas, and working/breathing losses are anticipated. A WAO test unit will likely require a RCRA (e.g., RD&D) permit if not permitted as part of the NPDES treatment system. There are no WAO-specific RCRA requirements that pertain to air emissions. However, there are certain general fugitive emissions requirements that could be applicable if the WAO is permitted under the 40 CFR 264, Subpart X criteria. If the WAO unit is sited at a location where it can be considered a stand-alone emission source, the state will likely require a construction permit and operating permit. If the unit is considered part of a larger facility (e.g., an AAP), the unit could require a PSD preconstruction permit modification and/or a Title V operating permit.

The sampling programs presented in Sections 5 and 6 for the WAO and CBC demonstration tests, respectively, were prepared in consideration of the information presented above and in Section 3.4 of the Regulatory Review Report.

3.3 Solid Wastes

Ash generated from the combustion of RCRA-listed (K047) red water would be classified as a K047 waste as defined by the "derived from rule." In addition to the K047 listing, the generator must also determine if the ash is a RCRA characteristic waste per 40 CFR 261, Subpart C. The RCRA characteristics include ignitability (D001), corrosivity (D002), reactivity (D003), and toxicity (D004-D043). The regulatory limits for these classifications are listed in 40 CFR 261, Subpart C. The ash could be landfilled as a hazardous waste in a RCRA-permitted hazardous waste landfill provided it meets the treatment standards in 40 CFR 268. If the ash has been delisted, it could be disposed in a nonhazardous waste (Subtitle D) landfill.

3.3.1 Hazardous Waste Landfill Disposal of Residue

One option for the final disposition of the K047 ash is disposal as a hazardous waste in a hazardous waste landfill (Subtitle C). Prior to land disposal, the ash must meet the land disposal restrictions in 40 CFR 268 for a K047 waste, and any applicable RCRA characteristics. The land disposal restrictions for K047 as listed in 40 CFR 268.42 require deactivation to remove the hazardous characteristic of reactivity from the ash. This is a technology-based standard and does not specify a concentration limit. Analysis of the following parameters are likely to be required to meet the waste characterization and disposal facility criteria:

- Explosivity
- Reactivity
- Landfill parameters (e.g., specific gravity; pH; cyanide; sulfide; phenolics; polychlorinated biphenyls; percent water; percent solids; flashpoint; total petroleum hydrocarbons; and toxicity characteristic leaching procedure for metals, volatiles, semivolatiles, pesticides, and herbicides).

Unless delisted, the ash must also be shipped as a hazardous waste. The generator must comply with the RCRA hazardous waste manifesting requirements (40 CFR 262) and DOT (49 CFR 171 to 199) hazardous materials shipping requirements.

For the purposes of this Test Plan, it is assumed that the ash may be sent to an offsite hazardous waste landfill for disposal.

3.3.2 Nonhazardous Waste Landfill Disposal of Residue

The second option for disposal of treated ash involves disposal in a nonhazardous waste landfill (Subtitle D). Prior to disposal in a nonhazardous landfill, the ash generated from the CBC process must be excluded from regulation by RCRA (delisted) by following the procedures described in 40 CFR 260.20 and 260.22. The delisting process requires the generator to demonstrate that the constituents for which the waste was listed and any other hazardous constituents (40 CFR 261, Appendix VIII) are not present in the waste at levels of regulatory concern and that the waste does not exhibit any of the characteristics of hazardous waste (i.e., ignitable, corrosive, reactive, or toxicity characteristics).

To demonstrate the nonhazardous nature of the treated waste, the generator must include in the delisting petition to EPA additional information, as outlined in "Petitions to Delist Hazardous

Waste A Guidance Manual" (EPA 530-R-43-007), to show that the waste will not be hazardous for other reasons. EPA evaluates the petition by using an analytical approach involving the modeling of the transport of toxic constituents from a landfill. The RCRA delisting process may take 18 to 24 months to complete and is cost effective only if significant volumes of waste are produced. Analytical parameters for the delisting process are anticipated to include those presented in 40 CFR 261, Appendix VIII.

For the purposes of this Test Plan, it is assumed that the ash disposal at nonhazardous waste landfill will be considered; that is, ash delisting will be considered to be an option.

4.0 Process Descriptions - Conceptual Designs

The following subsections present brief process descriptions of the WAO and CBC pilot-test units. The conceptual design reports present more detailed process descriptions as well as process flow diagrams, system controls, and the design basis. It should be noted that these process descriptions are based on the conceptual designs of these units and are subject to change during final design activities.

The conceptual designs represent generic WAO and CBC units and do not include vendor-specific or confidential information. However, certain WAO unit operations are facilitated by unique vendor approaches that are not shown or described. The final design should be prepared in consideration of the unique vendor approaches that are possible.

Both the WAO and CBC pilot-test units have been designed to be transportable; that is, they may be fabricated at a vendor location, loaded on trailers, transported to and reassembled at the test site. Because of the unique nature of the treatment processes, rental or lease equipment is not currently available.

4.1 *Wet Air Oxidation Demonstration Unit*

The pilot-scale WAO unit presented herein is a transportable system consisting of the following major components:

- Reactor section
- Reactor feed/effluent heat exchanger
- Reactor feed heater
- Effluent cooler
- Separators - high and low pressure
- Air compressor and accumulator
- Pumps - waste feed, dilution feed, high pressure feed, and effluent.

The WAO pilot-test unit is designed to treat 1.5 gallons per minute (gpm) of raw red water at a chemical oxygen demand (COD) level of 120,000 mg/L. The incoming red water will be diluted to a COD level of 60,000 mg/L with a treated effluent recycle stream because higher COD levels present safety concerns and cause excessive evaporation in the WAO unit. The design throughput after dilution of the feed stream is 3.0 gpm. Experimental data reported in Phull's dissertation (1992) predict a COD conversion in the 85 percent range at WAO reaction conditions of 485°F.

As reported in Phull's dissertation (1992), the corrosivity of red water is aggravated under process conditions of high temperature, high pressures, and low pH of oxidized solutions. Sulfonated nitroaromatics are expected to be more corrosive when subjected to WAO due to the formation of inorganic salts. On the basis of the corrosion testing performed by Phull, titanium was selected in the conceptual design as the material of construction for the WAO reactors and associated equipment and piping when the process temperature exceeds 100°F. For process effluent temperatures less than 100°F, equipment and piping may be constructed from 316 stainless steel.

The process conditions for the system described below are 484°F reaction temperature and 1000 psia. The following process description highlights the elements shown on the block flow diagram in Figure 4-1.

4.1.1 Feed Preparation and Preheat

Incoming red water from an onsite storage tank initially enters a mix tank where the pH is adjusted to 5. To prevent excessive evaporation in the WAO reaction section, the maximum COD concentration to be processed is adjusted to 6 percent (60,000 mg/L). This is achieved by blending the pH-adjusted red water with treated effluent at a preset ratio to yield a combined total of 3 gpm to the WAO unit.

The diluted feed then enters the tube-side of the reactor feed/effluent heat exchanger where the feed stream temperature is heated to the required inlet temperature by the heat present in the effluent from the reactors. During startup, an electric heater is necessary to heat the feed to the desired reaction temperature.

4.1.2 Reaction and Separation

The conceptual WAO pilot-test system consists of reactors connected in series. Compressed air is injected into the reactors to supply the required oxygen for the reaction.

The combined oxidized liquid and spent air is withdrawn from the reactors and cooled to 104°F in the reactor feed/effluent heat exchanger and effluent cooler. Gases and oxidized wastewater leave the cooler and enter a two-stage pressure let-down and separation system.

The off-gas being released from the pilot-scale reactor -- which is primarily carbon dioxide, nitrogen, and water vapor -- will be monitored to ensure that the air vented to the atmosphere is in compliance with regulatory limits. Approximately half of the oxidized wastewater is recycled to the inlet of the system and the remaining effluent will be discharged for treatment or disposal in accordance with regulatory permit requirements.

4.1.3 Compressed Air

Compressed air leaves a reciprocating compressor at a pressure of 1050 psia and is stored in an air accumulator prior to entering the WAO reactors. The total air flow to the WAO reactors is controlled by an oxygen analyzer, which measures the O₂ content of the off-gas leaving the system.

4.1.4 Facilities Support/Utility Requirements

The minimum utilities required for the operation of the WAO system are estimated to be:

- Electricity - 165 kilowatts
 - Voltage - 240/480
 - Max amps - 300 (full load)
 - Phases - 3
- Noncontact cooling water - 95 gpm
- Instrument air - 6.4 acfm at 100 psi.

It is estimated that the pilot-scale WAO unit will require an area sufficient for placement of two 40 ft by 8 ft trailers. Additionally sufficient space for placement of storage for untreated red water (influent) and treated effluent must be provided. The test area must be designed to meet the requirements of the RCRA permit. At a minimum, double containment must be provided to contain any leaks.

4.2 Circulating Bed Combustion Demonstration Unit

The pilot-scale CBC unit presented herein is a transportable incineration system consisting of the following major components shown on the block flow diagram in Figure 4-2:

- Feed system
- Combustion system
 - loop seal
 - circulating bed combustor (CBC)
 - hot cyclone

- Ash handling system
- Air pollution control system
 - partial quench
 - baghouse
 - induced draft (ID) fan
 - stack.

In general, red water is fed to the CBC where it is thermally treated. Combustion by-products (ash) and bed material are indirectly cooled with water in the ash cooler conveyor. The combustion gas is cooled in the partial quench and cleaned in the baghouse. Ash and bed material are discharged from the CBC by the ash cooler conveyor. The CBC off-gases are ducted to the partial quench where they are cooled to about 400°F. The cooled combustion gases pass through the baghouse where more than 99 percent of the particulate is removed. The cleaned combustion gases then pass through the induced draft fan and exit at the stack.

The CBC operating temperature of 1600°F is maintained by adding auxiliary fuel (natural gas) directly to the combustion chamber. The CBC system is designed to process 1.5 gpm of red water (heating value of 487 British thermal units per pound [Btu/lb]) with a heat release of 0.4 MMBtu/hr. The total thermal input to the system is 4 MMBtu/hr, which equates to a gas velocity of 20 feet per second (ft/sec) through the combustion chamber and an overall gas residence time of 2.2 seconds in the combustion system.

The following sections describe the feed system, combustion system, ash handling system, air pollution control system, and utility/facility requirements for the CBC unit in the conceptual design.

4.2.1 Feed System

The CBC unit has three major feed streams: red water, circulating media (e.g., aluminum oxide), and limestone (to reduce sulfur dioxide [SO₂] emissions). The red water and the circulating media are fed directly to the loop seal, from which the red water is volatilized and oxidized in the combustion chamber. Limestone is fed into the CBC above the main mass of the circulating bed.

Feed rates depend upon the contamination level in the waste feed and the expected O₂ and SO₂ levels in the combustion gas.

4.2.2 Combustion System

The combustion system is comprised of the following three regions: the loop seal, CBC, and hot cyclone. Red water enters at the loop seal prior to entering the combustion chamber. Inside the CBC, the red water is mixed and blended by the turbulence of the combustion air and the circulating media.

The CBC itself has the following elements:

- Windbox distributor/assembly - a refractory-lined carbon steel unit located in the lower portion of the CBC that receives combustion and circulating air; in addition a start-up burner is mounted in the wind box and has a maximum capacity of 5 MMBtu/hour
- Combustion chamber - a refractory-lined carbon steel vertical cylindrical chamber located above the distributor plate on the windbox
- Bed - located above the windbox assembly, the bed is comprised of bed materials and limestone that act as a large thermal flywheel for efficient heat transfer to the red water.

At temperatures greater than 1300°F, auxiliary fuel is fed directly to the CBC, where 4 MMBtu/hour of auxiliary fuel can be fed directly to the chamber. Primary air is provided to the start-up burner by the combustion air blower. Fluidizing air (secondary air) is fed directly to the wind box by the combustion air blower. The quantities of fuel and air fed to the CBC are carefully monitored and controlled to maintain the CBC combustion chamber flow rate and temperature.

Off-gases from the CBC, which include the bed material, enter a hot cyclone (to recover the bed material from the gases) before they are sent to the air pollution control system (APCS). The bed material is returned to the bottom of the CBC through a loop-seal that connects from the bottom of the cyclone to the CBC bed.

4.2.3 Ash Handling System

Ash and bed material are continuously purged from the combustion chamber and cooled by the ash cooler conveyor, which discharges the materials to the ash bin.

4.2.4 Air Pollution Control System

The APCS consists of a partial quench, baghouse, induced draft fan, and a stack.

Gases from the hot cyclone pass through a partial quench, which cools the gases to approximately 400°F in preparation for particulate removal in the baghouse. The baghouse removes more than 99 percent of the particulate entrained in the gas. After the baghouse, the gases enter an ID fan and exit through a stack.

4.2.5 Facilities Support/Utility Requirements

The minimum utilities required for the operation of the CBC unit include the following:

- Electricity
 - Voltage - 240/480
 - Max. amps - 225 Kva
 - Phases - 3
- Plant air - 928 scfm at 100 psi
- Instrument air
- Auxiliary fuel (natural gas) 4 MMBtu/h (182 lb/hr).

It is estimated that the pilot-scale CBC unit will require an area of approximately 120 ft by 50 ft and a storage area for four trailers. This does not include the feed storage and handling system. The entire area will have to be constructed to meet permit requirements. At a minimum, double containment will be required.

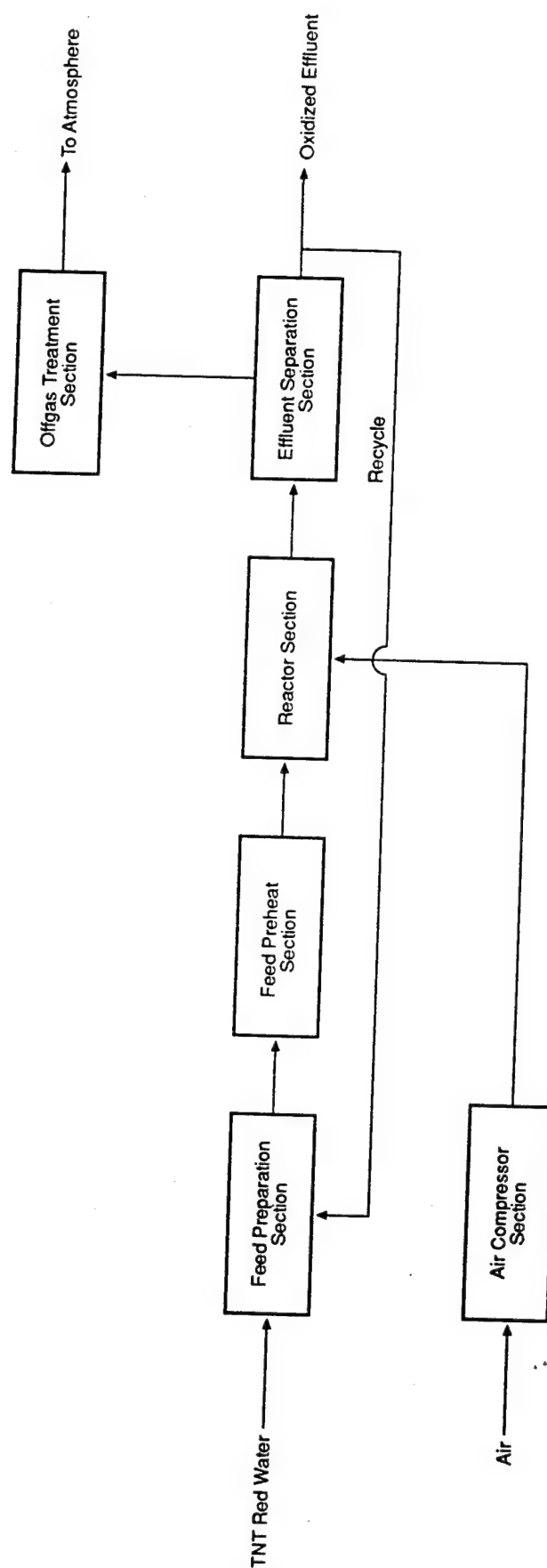
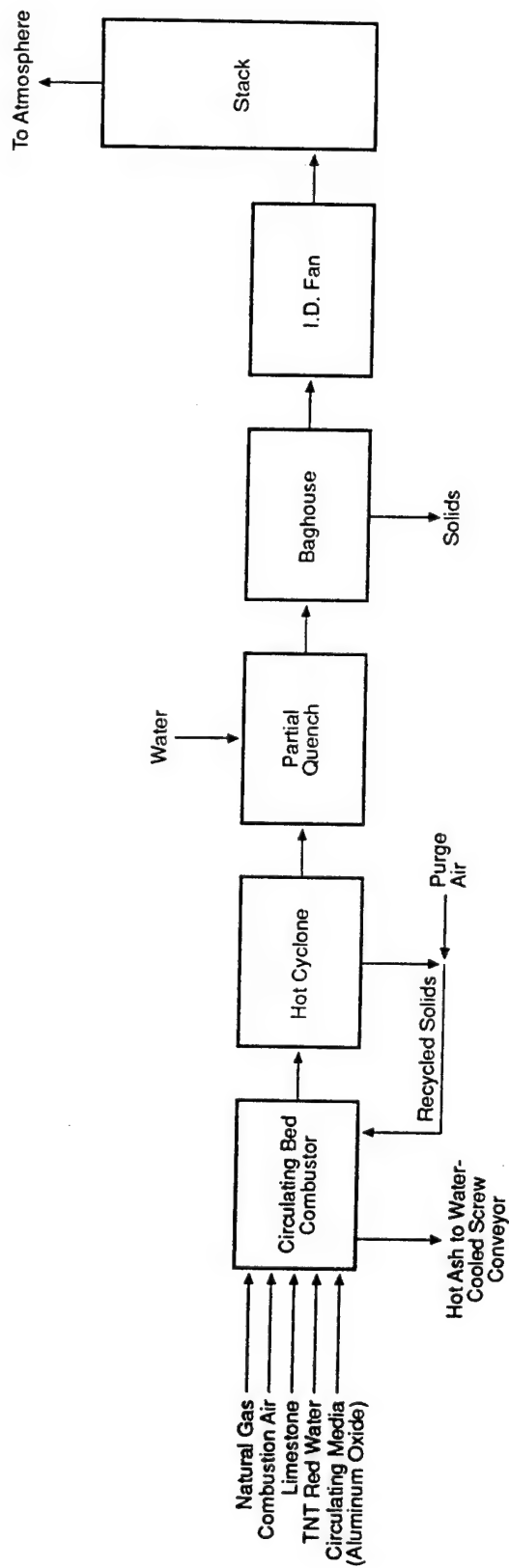


Figure 4-1.

WAO Test Unit Block Flow Diagram.

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	2/1/88	APPROVED BY	M-32243-S-1-1-295-D



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Figure 4-2.
CBC Test Unit Block Flow Diagram.

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	2/1/88	APPROVED BY		M-322243-S-1-1-295-D

5.0 WAO Demonstration Program

The following subsections describe the general program to demonstrate the effectiveness of the WAO treatment process.

5.1 Demonstration Program Overview

The demonstration program will consist of the following:

- Monitoring key system parameters
- Collecting and analyzing samples of process water and gases.

Operational conditions for the demonstration program are presented in Table 5-1. To optimize and assess the performance of the WAO unit, a series of six tests will be performed at varying red water flow rates, reactor pressures, and reactor temperatures; the impact of these parameters on a WAO system is described in Section 5.3.1, below. The test matrix in Table 5-1 was developed based on a review of the literature, equipment vendor recommendations presented in Section 12.0 (Sampling Plan) of the WAO Conceptual Design Report, and the preceding discussions regarding equipment designs and probable discharge criteria.

5.2 System Operation

A preliminary operations manual, including startup and shutdown procedures, for the pilot-scale WAO unit is presented in Section 13 of the WAO Conceptual Design Report. In general, startup consists of the following steps:

- Startup cooling system
- Activate instrument air system
- Fill the system with service water
- Increase system temperature
- Pressurize system
- Introduce wastewater feed stream
- Operate system after operating parameters have stabilized.

Because the steps presented above are not intended to be complete, the WAO operations manual should be used for all startup procedures.

5.3 Operating Parameters/Process Variables to be Monitored and Monitoring Locations

5.3.1 Process Monitoring

The primary control parameters for any WAO system, including that presented in the conceptual design, are:

- Feed rate - the feed rate to the WAO is limited by the size of the reactors and by the COD level as there is a correlation between flow rate and residence time.
- Oxygen flow (air demand) - the air supply may be optimized to ensure that the WAO unit is operating efficiently; the air demand is impacted by the COD and the feed rate.
- Reactor pressure - the pressure must be set so as to prevent boil-off and maintain a liquid phase in the reactors. The reaction enthalpy is used to:
 - preheat the red water to the reaction temperature
 - evaporate water to the vapor-liquid equilibrium
 - compensate for heat losses from the reactors.
- Reactor temperature - because the temperature determines the rate of the oxidation reaction, it is the most important process variable in a WAO unit. The required temperature is determined by the chemical composition of the red water and the desired conversion efficiency. For low COD materials, an electric heater is necessary.

As indicated in Section 12.4 of the WAO Conceptual Design Report, the pilot-test WAO unit presented in the conceptual design includes a distributed control system (DCS) to monitor the following:

- Flow rates of
 - raw red water
 - effluent recycle stream
 - diluted red water to the reactor system
 - air to the reactor system
 - air to the inlet of the feed/effluent heat exchanger
 - offgas air flow
- Oxygen content in the offgas line
- pH of the diluted red water to the reactor system
- Liquid levels in
 - feed tank
 - high pressure separator

- low pressure separator
- effluent tank
- Differential pressure across the strainer
- Pressures in
 - outlet line of the reactor system
 - high pressure separator vapor line
 - low pressure separator vapor line
- Temperatures of
 - feed at the tube-side outlet of the feed/effluent heat exchanger
 - outlet line of the reactor system
 - oxidized effluent at the outlet of the feed/effluent heat exchanger
 - oxidized effluent at the outlet of the effluent cooler
 - oxidized effluent in the effluent drum

The DCS will maintain a record of these process parameters throughout the test program.

5.3.2 Process Sampling

Process sampling to be performed for the WAO demonstration program consists of collecting samples from the following locations shown on Figure 5-1:

- Point 1 - incoming red water
- Point 2 - dilute red water
- Point 3 - oxidized effluent
- Point 4 - offgases.

To minimize safety hazards associated with the high pressures and temperatures in the reactor, no sample locations are located within the reactor system.

Analytical procedures for the collected samples are presented in Section 7. Sample identification, packaging, and shipping procedures are presented in Section 8.

5.4 Evaluation Criteria

The primary evaluation criteria for the WAO demonstration test are the following:

- Percent reduction in COD
- Percent reduction in Nitroaromatics

- Percent reduction in TNT
- Percent reduction in DNT.

Secondary evaluation criteria include the following:

- Offgas emissions
- Toxicity of the effluent
- Effluent characteristics (other than as defined above.)

The sampling program outlined in Table 5-2 has been designed to obtain the data necessary for these evaluations. Data validation and evaluation techniques are presented in Section 7 of this document.

Table 5-1 WAO Demonstration Test Operational Conditions

Test No. ¹	Description	Test Conditions				
		Red Water Flow Rate ² (gpm)	Reactor Pressure (psia)	Reactor Temperature (°F)	Diluted Red Water pH (S.U.)	Air Ratio (R101/R102)
Test Runs for Evaluating WAO System Performance						
1	Design	1.5	1000	484	8	50/50
2	50% System Turndown Capability	0.75	1000	484	5	50/50
Test Runs for Determining Optimal Operating Parameters for WAO						
3	Reduced reaction temperature and pressure	1.5	850	464	5	50/50
4	Reduced reaction temperature and pressure	1.5	750	446	5	50/50
5 :	pH adjustment	1.5	1000	484	"as-is"	50/50
6	Air flow ratio optimization	1.5	1000	484	5	60/40

¹ All tests to be 2 days in duration. Sampling as described on Table 5-2.

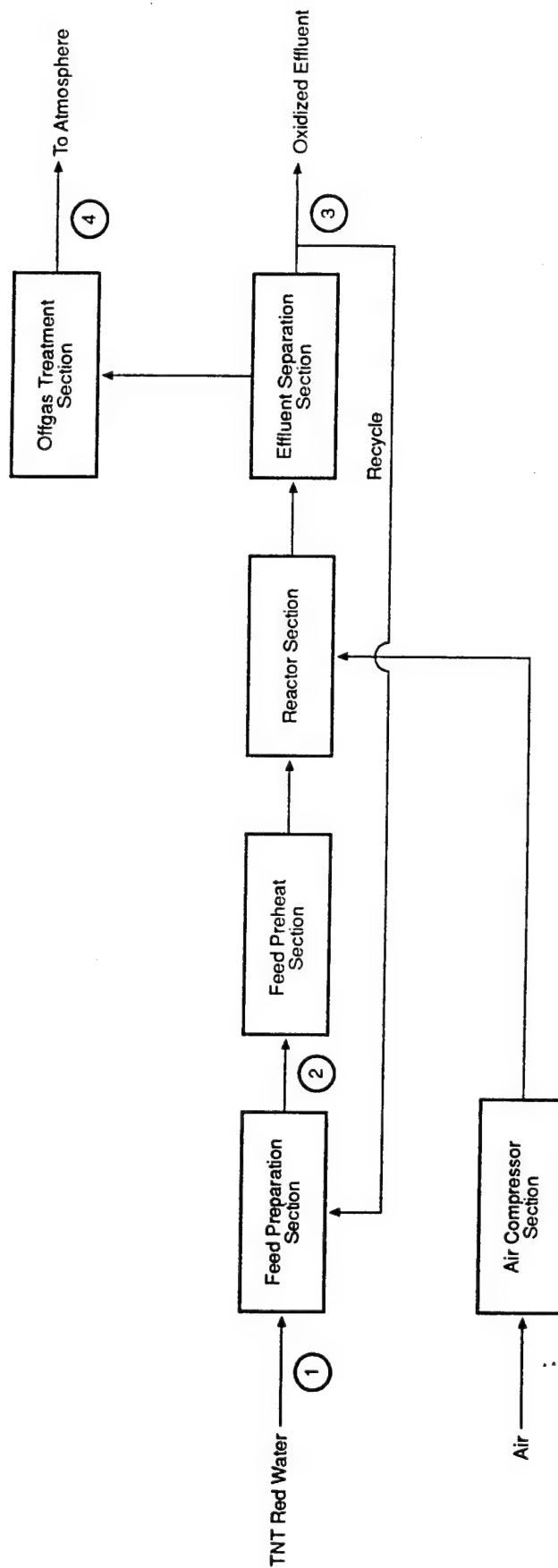
² Total feed (red water plus recycle) flow rate to be 3 gpm for all tests.

Table 5-2 WAO Demonstration Test Process Sampling Program

Sample Location ¹	Location Description	Required Analyses ²	Sample Type	Sampling Frequency
1	Raw red water	pH Chemical Oxygen Demand (COD) Biochemical Oxygen Demand (BOD ₅) Total Organic Carbon (TOC) Total Volatile Solids (TVS) Total Solids (TS) Total Dissolved Solids (TDS) Total Suspended Solids (TSS) Chlorides Nitroaromatics 2,4-Dinitrotoluene (DNT) 2,4,6-Trinitrotoluene (TNT) Nitrite Nitrate Sulfate	grab from tap	three times/day after steady-state conditions
2	Diluted red water	Raw red water parameters	grab from tap	same
3	Oxidized effluent	Raw red water parameters, plus Chronic Toxicity Acute Toxicity	grab from tap	same
4	Offgas	Carbon monoxide (CO) Carbon dioxide (CO ₂) Nitrogen oxide (NO) Ammonia (NH ₃) Oxygen (O ₂) Sulfur dioxide (SO ₂)	bag from port	same

¹ Sample locations shown on Figure 5-1.

² Analytical methods presented on Tables 7-1 and 7-2.



② Sample Location

Figure 5-1.
WAO Test Unit Sample Locations.

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6.0 CBC Demonstration Program

The following subsections describe the general program to demonstrate the effectiveness of the CBC treatment process.

6.1 *Demonstration Program Overview*

The demonstration program will consist of the following:

- Monitoring key system parameters
- Collecting and analyzing samples of ash and gases.

Operational conditions for the demonstration program are presented in Table 6-1. To optimize and assess the performance of the CBC unit, a series of six tests will be performed and varying red water flow rates, CBC gas velocities, and CBC bed depths; the impact of these parameters on a CBC system is described below. The test matrix in Table 6-1 was developed based on review of the recommendations in the following sections of the CBC Conceptual Design Report:

- Section 14.0 (Recommended Tests and Analyses) - presents a series of tests to be conducted on the following parts of the treatment system
 - CBC unit (e.g., optimizing bed depth, selecting bed material, assessing limestone as a neutralizing agent, evaluating impact of steam in the circulating bed, evaluating system turn down capacity, evaluating system performance, finalizing start-up burner location, and determining the optimum gas velocity in the CBC)
 - Hot cyclone unit (e.g., evaluating cyclone/loop-seal performance)
 - Air pollution control system (e.g., determining the optimum air/cloth ratio in the baghouse, and evaluating whether the bags should be precoated with lime)
- Section 16.0 (Sampling Plan) - presents tests to be conducted to demonstrate the performance of the CBC and air pollution control equipment
- Section 18.0 (Performance Test Plan) - combines the sampling programs of Sections 14.0 and 16.0; forms the basis for the sampling program presented herein.

It should be noted that many of the tests outlined in the CBC Conceptual Design Report are observational in nature and are not specifically included in this Test Plan. The CBC Conceptual Design Report should be reviewed in preparation for the CBC demonstration test program.

Specifically, the following parameters will be studied during the CBC performance tests (and formed the basis for the test program in Table 6-1):

- Evaluate system performance - during the test program, the operational performance relative to regulatory and warranted performance criteria. From these tests, the maximum waste feed rate may be determined.
- Optimal bed depth - during the test program, the impact of variations in the bed depth (measured as the pressure drop across the combustion chamber) on the performance of the CBC and the APCS will be studied and the optimum pressure ranges determined. If the bed depth is too low, the CBC bed material will not circulate properly and heat transfer will be low. If the bed depth is too high, greater quantities of bed materials will be carried over to the APCS, increasing the particulate burden to the APCS and requiring frequent addition of fresh bed material to the combustion chamber. In addition, the pressure will be too great for the ID fan to exhaust gases through the stack.
- Optimum gas velocity in the CBC - during the test program, the impact of variations in the gas velocity in the combustion chamber on the performance of the CBC and APCS will be studied and the optimum operational ranges determined. If the gas velocity is too low, the CBC bed material will not circulate properly. If the gas velocity is too high, greater quantities of bed materials will be carried over to the APCS, increasing the particulate burden to the APCS and requiring frequent addition of fresh bed material to the combustion chamber.
- Loop-seal performance - during the test program, the performance of the loop-seal at varying loop-seal fluidizing flow rates will be assessed.
- Optimum air to cloth ratio in the baghouse - during the test program, the impact of the variations in the air to cloth ratio on baghouse performance will be determined. By closing off a baghouse module, the air to cloth ratio in the baghouse can be varied.
- Appropriate bed material selection - during the test program, the selected bed material will be tested for resistance to abrasion and the formation of eutectic mixtures. The optimum bed material is resistant to abrasion and do not form low melting point eutectics. Bed materials that are not resistant to abrasion will increase the particulate burden to the APCS and require frequent additions of bed material to the CBC. Bed materials that are comprised primarily of salts will chemically combine with components in the waste feed to form low melting point materials. These low melting point materials will lead to the solidification of the bed material, and the resulting shutdown of the CBC for removal of the aggregate solid bed material.
- Use of limestone to reduce sulfur dioxide (SO₂) emissions - during the test program, the SO₂ emissions will be measured and compared to regulatory criteria. If the SO₂ emissions are greater than the regulatory criteria, then the impact of limestone addition

to the SO₂ emissions will be studied and a decision made on whether to add limestone to the bed material or to inject lime slurry into the quench. The quantity of limestone or lime slurry will also be determined.

- System turndown capability - during the test program, the ability of the CBC to operate in a stable manner at varying feed rates will be studied. From this study, the minimum waste feed rate will be determined.
- Precoating the baghouse bags with lime - during the test program, tests will be conducted to determine if the baghouse bags should be precoated with lime to increase the operational reliability of the baghouse. The high moisture of the combustion gases may cause poor baghouse operational reliability.

6.2 CBC System Start-Up

The procedures in this section are excepted from Section 17.0 of the CBC Conceptual Design Report and are supplements to the procedures that will be described in the equipment vendors' manual. The procedures in the vendors' manuals and in Section 17.0 of the CBC Conceptual Design Report should be consulted and followed as appropriate.

The following utilities must be available before attempting to start the CBC:

- Electrical power - normal and uninterrupted power supply (UPS)
- Instrument air
- Plant air
- Auxiliary fuel - natural gas.

6.2.1 Cold Start Procedure Summary

The following summary procedure assumes that the CBC refractory does not require curing:

1. Check that the ash system is operational.
2. Start the combustion air blower (B-2001) by pushing the start button (HS-204).
3. Start the ID fan (B-5001) by pushing the start button (HS-501).
4. Start the loop-seal blower (B-2002) by pushing the start button (HS-207).
5. Add the bed material to the CBC until the differential pressure across the bed is more than 20 in. w.c. on PDIT-206.
6. Check that water is available to the quench.
7. Check that process air is available to the baghouse.

8. Light the start-up burner by pressing the start button.
9. Gradually increase natural gas flow manually to the start-up burner according to the recommended refractory heat up schedule.
10. When the CBC reaches 1300°F, put the start-up burner in manual (FIC-209).
11. Initiate the flow of primary fuel to the CBC by pressing HS-219.
12. Gradually increase the flow of primary fuel (FIC-219) to the CBC until the start-up burner is at low-fire.
13. Shut off the start-up burner.
14. Increase primary fuel firing rate manually until all normal operating set points are met (e.g., 1600°F in the CBC combustion chamber temperature).
15. After all set points are met, start the red water feed at a reduced rate. Monitor CBC combustion chamber temperature manually by adjusting the primary auxiliary fuel firing rate using FIC-219. Watch for slagging and overheating of the CBC.
16. Gradually increase the red water feed rate while monitoring the stack gas oxygen concentration. The maximum red water feed rate will be obtained when the feed rate is equal to the permit feed limit or the stack oxygen concentration is equal to 3 percent oxygen.
17. Adjust TIC-203 output to agree with FIC-219 set point, and switch FIC-219 to automatic/cascade control. Switch TIC-203 to automatic/local with its set point agreeing with the exit gas temperature. TIC-203 will then modulate the set point to FIC-219 to increase or decrease the firing rate to the start-up burner to maintain CBC off-gas temperature at the set point.

6.2.2 Hot Start Procedure Summary

After an emergency shutdown, the CBC can be restarted as follows:

1. Check that all combustion air blowers are operating.
2. Check that the CBC ancillary equipment is operating.
3. Re-light the start-up burner.
4. Re-establish CBC temperature and waste feed rate by following the last eight steps in Section 6.2.1, Cold Start Procedure Summary.

6.2.3 Start-Up During Hot Idle

To start-up from hot idle, follow Steps 10 through 17 of Section 6.2.1, Cold Start Procedure Summary.

6.3 Operating Parameters/Process Variables to be Monitored and Monitoring Locations

6.3.1 Process Monitoring

The Conceptual Design for the demonstration CBC unit includes a programmable logic controller (PLC) to monitor the following:

- Air temperature at the following locations
 - combustion chamber
 - before the cyclone
 - before the quench
 - before the baghouse
- Temperature of water from the ash conveyor
- Stack gas concentrations of
 - oxygen
 - carbon monoxide
- Flow rates of
 - auxiliary fuel
 - combustion air
 - combustion gas
 - combustion gas in the combustor
 - stack gas
- Pressure drops across
 - the distributor plate
 - the bed
 - the baghouse.

The PLC will maintain a record of these process parameters throughout the test program.

6.3.2 Process Sampling

Process sampling to be performed for the CBC demonstration program consists of collecting samples from the following locations shown on Figure 6-1:

- Location 1 - incoming red water

- Location 2 - CBC bed ash
- Location 3 - baghouse ash
- Location 4 - stack offgases using a multi-metals sampling train (MMT)
- Location 5 - stack offgases using an EPA Modified Method 5 (MM5) sampling train
- Location 6 - stack offgases using a volatile organic sampling train (VOST)
- Location 7 - stack offgases using an EPA Method 0050 sampling train
- Location 8 - stack offgases using continuous emission monitors (CEMs)
- Location 9 - stack offgases using a cascade impactor.

No sample locations are located within the CBC system to minimize safety hazards associated with the high temperatures in the CBC.

Analytical procedures for the collected samples are presented in Section 7. Sample identification, packaging, and shipping procedures are presented in Section 8.

6.4 Evaluation Criteria

The objective of the CBC demonstration test is to obtain data that will:

- Demonstrate greater than 99.99 percent destruction in principal organic hazardous constituents (POHCs)
- Confirm the fate of POHCs fed to the CBC; determine if they are destroyed by thermal oxidation or emitted in the stack gases, ash residues, or scrubber purge stream
- Demonstrate that the emissions of carbon monoxide (CO) are less than 100 parts per million, volume (ppmv) corrected to 7 percent oxygen (O₂); or, if the stack gas CO is greater than 100 ppmv corrected to 7 percent O₂, the stack gas concentrations of THC do not exceed 20 ppmv
- Demonstrate control of particulate emissions to less than 0.015 grains per dry standard cubic foot (gr/dscf) corrected to 7 percent O₂
- Demonstrate compliance with the hydrochloric acid gas (HCl), chlorine (Cl₂), and sulfur dioxide (SO₂) emission standards
- Determine the emission rates of speciated volatile and semivolatile organics

- Demonstrate compliance with the metals emissions criteria
- Determine the emission rates of O₂, CO, THC, and nitrogen oxides (NO_x)
- Provide process information necessary to determine the suitability of the CBC in the destruction of red water
- Demonstrate compliance with RCRA and other regulatory performance requirements.

The demonstration test sampling program outlined in Table 6-2 has been designed to obtain the data for these evaluations. Data validation and evaluation techniques are presented in Section 7 of this document.

Table 6-1 CBC Demonstration Test Operational Conditions

Test No. ¹	Description	Test Conditions		
		Red Water Flow Rate (gpm)	CBC Gas Velocity (ft/sec)	Bed Depth (ft)
Test Runs for Evaluating CBC System Performance				
1	Design	1.5	20	6
2	Reduced flow	0.75	20	6
Test Runs for Determining Optimal Operating Parameters for CBC				
3	Reduced gas velocity	1.5	15	6
4	Increased gas velocity	1.5	25	6
5	Reduced bed depth	1.5	20	4
6	Increased bed depth	1.5	20	8

¹ All tests assumed to be 4 hours in duration. Sampling as described on Table 6-2.

Table 6-2 CBC Demonstration Test Process Sampling Program

Sample Location ¹	Location Description	Sample Matrix	Required Analyses ²	Sample Type	Collection Method ³	Sampling Frequency
1	Raw red water	Liquid	Density	grab from tap	SW-846 methods	every 15 minutes
			Heat content			
			Ash content			
			Total chlorine			
2	CBC ash	Solid	Semivolatile organic compounds (SVOCs)	composite	SW-846 methods	every 15 minutes
			Metals			
			SVOCs	grab from chute	SW-846 methods	every 15 minutes
3	Baghouse ash	Solid	Metals	composite	SW-846 methods	each run
			Salts (inorganic)			
			SVOCs	grab from baghouse	SW-846 methods	hourly after steady state
4	Stack gas	Gas	Metals	composite	SW-846 methods	each run
			Salts (inorganic)			
			Moisture	composite from port	EPA 4 BIF 0012 EPA 3 EPA 3 EPA 2	each run
			Metals			
			Oxygen (O ₂)			
			Carbon dioxide (CO ₂)			
			Velocity, pressure, temperature			

¹ Sample locations shown on Figure 6-1.

² Analytical methods presented on Tables 7-1, 7-2, and 7-3.

³ SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986. EPA denotes methods in "Sampling and Analysis Methods for Hazardous Waste Combustion," EPA 600/8-84-002.

BIF denotes methods presented in 40 CFR, Appendix B, "Federal Register," Volume 54 No. 206, October 1989, and the "Methods Manual for Compliance with BIF Regulations Burning Hazardous Waste in Boilers and Industrial Furnaces," USEPA, December 1990.

NSPS denotes methods in "New Source Performance Standards," Test Methods and Procedures, 40 CFR 60, Appendix A.

Table 6-2 (continued)

Sample Location ¹	Location Description	Sample Matrix	Required Analyses ²	Sample Type	Collection Method ³	Sampling Frequency
5	Stack gas	Gas	Moisture SVOCs Dioxins/furans O ₂ CO ₂ Velocity, pressure, temperature	composite from port	EPA 4 SW-846 0010 EPA 23 EPA 3 EPA 3 EPA 2	each run
6	Stack gas	Gas	Volatile organic compounds (VOCs)	composite from port	SW-846 0030	four composite samples (tube sets)/run
7	Stack gas	Gas	Moisture Hydrochloric acid (HCl) Chlorine (Cl ₂) Particulate O ₂ CO ₂ Velocity, pressure, temperature	composite from port	EPA 4 BIF 0050 BIF 0050 EPA 5 EPA 3 EPA 3 EPA 2	each run
8	Stack gas	Gas	O ₂ Carbon monoxide (CO) Sulfur oxides (SOx) Nitrogen oxides (NO _x)	continuous monitor from port	NSPS 3A NSPS 10 NSPS 6C NSPS 7E	continuous during runs
9	Stack gas	Gas	Cascade impactor - particulate	composite from port	Cascade impactor	periodic during runs

¹ Sample locations shown on Figure 6-1.

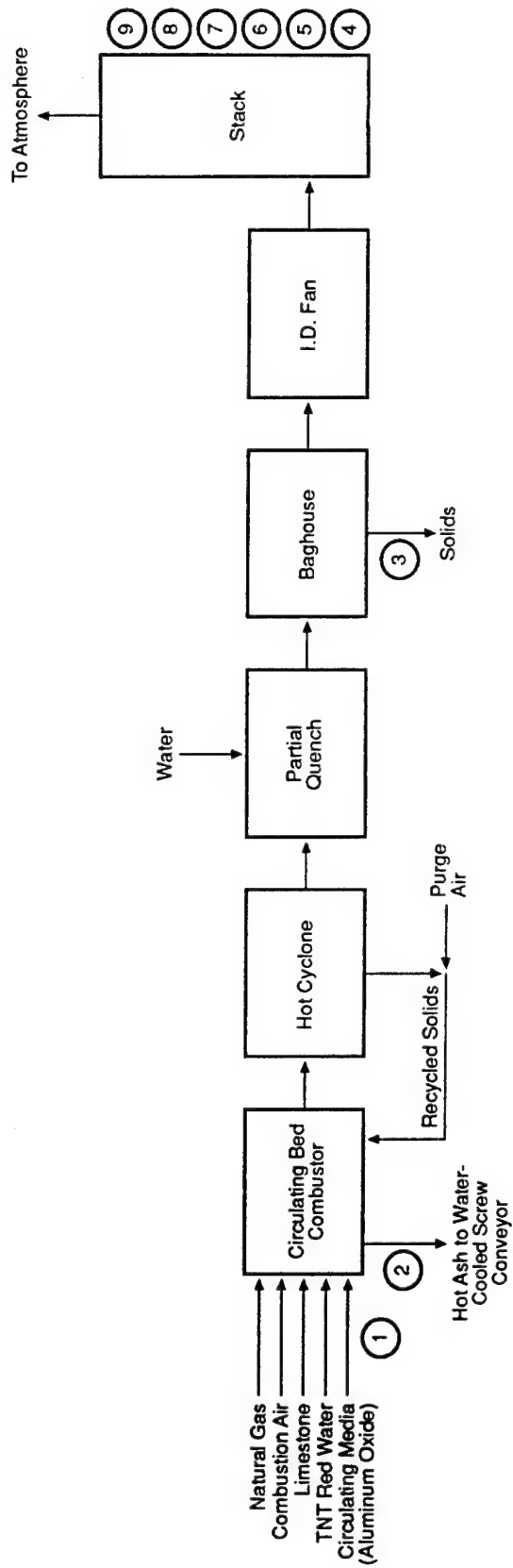
² Analytical methods presented on Tables 7-1, 7-2, and 7-3.

³ SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986.

EPA denotes methods in "Sampling and Analysis Methods for Hazardous Waste Combustion," EPA 600/8-84-002.

BIF denotes methods presented in 40 CFR, Appendix B, "Federal Register," Volume 54 No. 206, October 1989, and the "Methods Manual for Compliance with BIF Regulations Burning Hazardous Waste in Boilers and Industrial Furnaces," USEPA, December 1990.

NSPS denotes methods in "New Source Performance Standards," Test Methods and Procedures, 40 CFR 60, Appendix A.



② Sample Location

Figure 6-1.
CBC Test Unit Sample Locations.

DRAWING BY	JEM 1/23/88	CHECKED BY	APPROVED BY	DRAWING NO. M-322243-5-1-1-1/95-D
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7.0 Analytical Methods and Quality Assurance

7.1 Analytical Methods

The analytical methods that will be used for the red water demonstration tests outlined in this Test Plan are presented in the following:

- "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986
- "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, Revised March 1993
- "Procedure Manual, Chemical Laboratories, Technical and Quality Assurance Department, Hercules Incorporated, Radford Army Ammunition Plant, Radford, Virginia," issue date 05/93
- "Standard Methods for the Examination of Water and Wastewater," 18th ed., 1992; American Public Health Association, American Water Works Association, and the Water Environment Federation
- Methods published by "American Society for Testing and Materials"
- 40 CFR, Appendix B, "Federal Register," Volume 54 No. 206, October 1989, and the "Methods Manual for Compliance with BIF Regulations Burning Hazardous Waste in Boilers and Industrial Furnaces," U.S. EPA, December 1990
- "New Source Performance Standards," Test Methods and Procedures, 40 CFR 60, Appendix A.

Specific analytical methods for aqueous, gas, and solid samples are presented on Tables 7-1, 7-2, and 7-3, respectively, for the parameters presented in Tables 5-2 and 6-2.

It is anticipated that the analyses will be performed by the host facility's analytical laboratory. Samples will be submitted for analyses in accordance with the host facility's protocol and regulations and the procedures presented in Section 8 of this document.

A selected subgroup of samples (approximately 10 percent) may be shipped off-site for confirmatory analyses. These samples will be submitted for analyses in accordance with the procedures in Section 8 of this document. These off-site confirmatory samples will be analyzed on split samples from the test units at a frequency of approximately 1 in 10. The objective of

these off-site analyses is to verify the effectiveness of the technologies being demonstrated (e.g., percent reduction in COD attributable to WAO) or assess the attainment of various discharge criteria (e.g., air emissions from the CBC).

7.2 Quality Objectives

The objective of this project is to evaluate the effectiveness of the WAO and CBC in treating red water from TNT production. The red water that will be used in the demonstration tests is anticipated to contain approximately 15 percent dissolved solids (150,000 ppm), consisting of the following:

- 7 percent inorganic salts (e.g., sodium sulfite, sodium sulfate, sodium nitrite, sodium nitrate)
- 8 percent sodium salts of dinitrotoluene sulfonic acids.

An initial analysis of the red water before treatment will determine the compounds of interest for the demonstration tests and their concentrations in the red water.

7.2.1 WAO Mass Balance

A mass balance will be calculated for each compound of interest in the WAO treatment process using the following expression:

$$MC_{in} = MC_{og} + MC_{ls} + MC_{dc}$$

where:

MC_{in} = Mass of the compound entering the process in the waste feed stream (kg)

MC_{og} = Mass of the compound exiting the process in the off-gas (kg) (where applicable)

MC_{ls} = Mass of the compound in the liquid effluent (kg)

MC_{dc} = Mass of the compound destroyed or created in the WAO process (kg).

The mass of the compound the waste feed stream, the off-gas stream, and the liquid effluent will be calculated as the product of the concentration ^o of the compound and the volume (V) of the stream:

$$MC_{in} = C_{in} \times M_{in}$$

$$MC_{og} = C_{og} \times M_{og}$$

$$MC_{ls} = C_{ls} \times M_{ls}$$

where:

C_{in} = Concentration of the compound in the waste feed stream (kg/kg of sample)

M_{in} = Mass of the sample of the waste feed stream entering the process (kg of sample)

C_{og} = Concentration of the compound in the off-gas (kg/kg of sample) (where applicable)

M_{og} = Mass of the sample of off-gas exiting the process (kg) (will require conversion from m³/hr to kg/hr by multiplying by the gas density in kg/m³)

C_{ls} = Concentration of the compound in the liquid stream exiting the system (kg/kg of sample)

M_{ls} = Mass of the sample of liquid stream exiting the process (kg of sample).

7.2.2 CBC Mass Balance

A mass balance will be calculated for each compound of interest in the CBC treatment process using the following expression:

$$MC_{in} = MC_{sg} + MC_{bd} + MC_{ba} + MC_{dc}$$

where:

MC_{in} = Mass of the compound entering the process in the waste feed stream (kg)

MC_{sg} = Mass of the compound exiting the process in the stack gas (kg) (where applicable)

MC_{bd} = Mass of the compound exiting the process in the baghouse dust (kg) (where applicable)

MC_{ba} = Mass of the compound exiting the process in the CBC bed ash (kg) (where applicable)

MC_{dc} = Mass of the compound destroyed in the combustion process (kg).

The mass of the compound in the waste feed stream, the stack gas stream, and the baghouse dust, and the CBC bed ash will be calculated as the product of the concentration of the compound and the mass of the stream:

$$MC_{in} = C_{in} \times M_{in}$$

$$MC_{sg} = C_{sg} \times M_{sg}$$

$$MC_{bd} = C_{bd} \times M_{bd}$$

$$MC_{ba} = C_{ba} \times M_{ba}$$

where:

C_{in} = Concentration of the compound in the waste feed stream sample (kg/kg of sample)

M_{in} = Mass of the waste feed stream sample (kg of sample)

C_{sg} = Concentration of the compound in the stack gas (kg/kg of sample) (where applicable)

M_{sg} = Mass of the stack gas samples (kg) (will require conversion from m³/hr to kg/hr by multiplying by the gas density in kg/m³)

C_{bd} = Concentration of the compound in the baghouse dust (kg/kg of sample) (where applicable)

M_{bd} = Mass of the baghouse dust sample (kg of sample)

C_{ba} = Concentration of the compound in the CBC bed ash (kg/kg of sample) (where applicable)

M_{bd} = Mass of the CBC bed ash sample (kg of sample).

7.3 Calculation of Results

Analytical results will be calculated by the appropriate equations and reported in the appropriate concentration units. Data reduction of analytical results will be performed by the analyst and checked by a Senior Technical Reviewer.

The Senior Technical Reviewer will be responsible for validating the quality of the data generated by the laboratory with respect to the Quality Assurance Objectives. If these objectives are not met, the Senior Technical Reviewer is responsible for flagging the suspect data. An independent and/or external check will also be conducted in addition to this review. The lab data report should describe the probable reasons the data are considered suspect.

The Project Team will examine the data to verify that all measurements are within the specified ranges or are flagged as suspect and accompanied by a description of the reasons they are suspect. The team will then examine the data for any gross inconsistency with known experimental conditions. If an inconsistency is found, the source of the inconsistency will be investigated and an explanation will be provided.

7.4 Internal Quality Control

A system of quality control (QC) checks will be used to ensure that the data output meets prescribed data quality criteria and are consistent with the EPA Guidance and Requirements documents that are in-force at the time of the pilot demonstrations. The analytical QC program will use the following QC analyses to control and assess data quality:

- Laboratory control standards
- Method blanks
- Matrix spikes/matrix spike duplicates (MS/MSD).

Laboratory control standards (LCS) are standard reference solutions or laboratory pure-water spikes. These standards will be used to ensure that the instrument or procedure is within control limits before the samples are analyzed. Internal control limits are set for each analyte, and results of an LCS run are recorded and checked to ensure it is within control limits before any sample analysis is begun.

A method blank is a sample of laboratory deionized water carried through the entire preparation and analysis procedure. The method blank results and the sample results will be reported. A method blank will be run with each analysis batch.

As designated in specific analytical method(s) and/or regulatory requirements, MS and MSD samples will be prepared and analyzed at an appropriate frequency (e.g., one in every 20 samples). Random samples may also be spiked to determine accuracy as a percentage of recovery of the analyte from the sample matrix. In this case, samples will be randomly selected and split into identical triplicates, two of which will be spiked with a known mass of the analyte. The MS and MSD samples will be prepared using reagent grade salts, pure compounds, or certified stock solutions whenever possible; concentrated solutions will be used to minimize differences in the sample matrix resulting from dilution. Typically USEPA-recommended matrix spiking solutions will be used to assess matrix effects. Deviations from the established QC criteria for the

analytical method or regulatory requirement will be noted and reanalysis or other corrective action will be instituted as appropriate for the situation.

Reagents used in the laboratory are normally of analytical reagent grade or higher purity. All reagents are labeled with the date received and date opened. Deionized water quality is routinely checked.

7.5 Calculation of Data Quality Indicators

This section describes how the data quality indicators will be calculated. Equations have been provided for the calculation of precision, accuracy, method detection limits, and metals mass balances. Tables 7-1, 7-2, and 7-3 present the QA objectives for precision, accuracy, and method detection limits (MDL).

7.5.1 Precision

Duplicate analyses result will be used to evaluate the precision of an analysis. Results of these analysis will be used to determine the relative percent difference (RPD) between the replicate samples as calculated by the following equation:

$$RPD = \frac{(Rsa - Rdup)}{0.5 \times (Rsa + Rdup)}$$

where:

Rsa = Recovery of the sample

Rdup = Recovery of the duplicate.

7.5.2 Accuracy

Accuracy can be estimated by calculating the percent recovery of laboratory matrix spike and matrix spike duplicate samples using the following equation:

$$\% \text{ Recovery} = \frac{\text{spiked aliquot concentration} - \text{unspiked aliquot concentration}}{\text{amount of spike added}}$$

The percent recovery of the laboratory control sample will be calculated using the following equation:

$$\% \text{ Recovery} = 100 \times \frac{C_m}{C_{sm}}$$

where:

C_m = measured concentration of LCS

C_{sm} = actual concentration of LCS.

7.5.3 Method Detection Limit (MDL)

Method Detection Limits (MDLs) are the minimum concentrations of a substance that can be measured and reported with 99 percent confidence that the value is above zero. Prior to the start of the sampling program, the MDLs for the critical target parameters for each analytical method will be verified according to the protocol established in SW846, 3rd Edition, Section I, QC. The MDL reported for each sample will be determined by the calculated MDL, the appropriate dilution/concentration factors dictated by the sample preparation methods, and any extract dilutions necessary to adjust the analyte concentrations to the calibration ranges of the respective instruments.

7.6 Impact of Not Meeting QA Objectives

The QA objectives outlined in Tables 7-1, 7-2, and 7-3 were set to ensure that the data gathered during the project is of the highest quality. The data will be initially checked by the analyst to determine if the data are within the specified ranges set forth in Table 7-1. Data for all measurements will be evaluated in relation to the QA objectives of this study as soon as available so that the appropriate corrective action(s) can be immediately implemented. Examples of corrective actions include reviewing calculations for errors, examining measurement equipment and instruments for problems, repeating the experiment in question, or checking the validity of calculations. When feasible, the measurement will be repeated until the measurement system is in control.

If QA objectives are not met after the corrective action has been taken, the data will be qualified and a discussion will be included in the project report that outlines the overall impact to the project of not meeting the objectives. The discussion will address, as appropriate:

- 1) possible sources of bias or variability that affect the data
- 2) inadequacies of the techniques used to assess precision and accuracy
- 3) limitation of the measurement methods used.

Table 7-1 Red Water Demonstration Tests Analytical Methods - Water Samples

Analyte ¹	Analytical Method	Reference ²	Measurement Units	Minimum Detection Limit (MDL)	Precision (RPD) ³	Accuracy (% recovery) ⁴
pH	9040	SW-846	standard units	NA	NA	NA
COD	410.1	EPA	mg/L	20	<25	Control charted
BOD	405.1	EPA	mg/L	NA	NA	NA
TOC	415.1	EPA	mg/L	1	<25	Control charted
TVS	160.4	EPA	mg/L	1	<25	Control charted
TS	160.3	EPA	mg/L	1	<25	Control charted
TDS	160.1	EPA	mg/L	1	<25	Control charted
TSS	160.2	EPA	mg/L	1	<25	Control charted
Chlorides	325.3	EPA	mg/L	0.5	<25	Control charted
Nitroaromatics	8330	SW-846	ug/L	variable	<20	Control charted
2,4-DNT	8330	SW-846	mg/L	0.1	25	80-120

¹ Acronyms presented on Tables 5-2 and 6-2; NA denotes not applicable; NSIM denotes not specified in method.

² SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986.

EPA denotes methods listed in "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, Revised March 1993.

Hercules denotes methods presented in "Procedure Manual, Chemical Laboratories, Technical and Quality Assurance Department, Hercules Incorporated, Radford Army Ammunition Plant, Radford, Virginia," issue date 05/93.

SM denotes methods listed in "Standard Methods for the Examination of Water and Wastewater," 18th ed., 1992; American Public Health Association, American Water Works Association, and the Water Environment Federation.

ASTM denotes methods published by "American Society for Testing and Materials."

³ Precision given as Relative Percent Difference of duplicate samples unless otherwise indicated.

⁴ Accuracy given as percent recovery of MS, unless otherwise indicated.

Table 7-1 (continued)

Analyte ¹	Analytical Method	Reference ²	Measurement Units	Minimum Detection Limit (MDL)	Precision (RPD) ³	Accuracy (% recovery) ⁴
2,4,6-TNT	8330	SW-846	mg/L	0.1	25	80-120
Nitrite	4500-NO ₂ -C	SM	mg/L	NSIM	<35	80-120
Nitrate	9200	SW-846	mg/L	NSIM	<35	80-120
Sulfate	4500-SO ₄ -B	SM	mg/L	NSIM	<35	80-120
Acute toxicity	Acute toxicity (600 4-90-027)	EPA	acute toxicity units	NSIM	<35	80-120
Chronic toxicity	Chronic toxicity (600 4-90-001)	EPA	chronic toxicity units	NSIM	<35	80-120
Density	D-1429	ASTM	g/cc	NA	NA	NA
Heat content	D-2015	ASTM	BTU/lb	NA	NA	NA
Ash content	D-482	ASTM	%	NA	NA	NA
Total chlorine	4500-Cl F/G	SM	ug/L	50	<35	70-130

¹ Acronyms presented on Tables 5-2 and 6-2; NA denotes not applicable; NSIM denotes not specified in method.

² SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986.

EPA denotes methods listed in "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, Revised March 1993.

Hercules denotes methods presented in "Procedure Manual, Chemical Laboratories, Technical and Quality Assurance Department, Hercules Incorporated, Radford Army Ammunition Plant, Radford, Virginia," issue date 05/93.

SM denotes methods listed in "Standard Methods for the Examination of Water and Wastewater," 18th ed., 1992, American Public Health Association, American Water Works Association, and the Water Environment Federation.

ASTM denotes methods published by "American Society for Testing and Materials."

³ Precision given as Relative Percent Difference of duplicate samples unless otherwise indicated.

⁴ Accuracy given as percent recovery of MS, unless otherwise indicated.

Table 7-1 (continued)

Analyte ¹	Analytical Method	Reference ²	Measurement Units	Minimum Detection Limit (MDL)	Precision (RPD) ³	Accuracy (% recovery) ⁴
SVOCs	8270	SW-846	ug/L	10	< 30	70-130
Metals	3010/6010 7470	SW-846 SW-846	mg/L	NSIM	< 35	80-120

¹ Acronyms presented on Tables 5-2 and 6-2; NA denotes not applicable; NSIM denotes not specified in method.

² SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986.

EPA denotes methods listed in "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, Revised March 1993.

Hercules denotes methods presented in "Procedure Manual, Chemical Laboratories, Technical and Quality Assurance Department, Hercules Incorporated, Radford Army Ammunition Plant, Radford, Virginia," issue date 05/93.

SM denotes methods listed in "Standard Methods for the Examination of Water and Wastewater," 18th ed., 1992; American Public Health Association, American Water Works Association, and the Water Environment Federation.

ASTM denotes methods published by "American Society for Testing and Materials."

³ Precision given as Relative Percent Difference of duplicate samples unless otherwise indicated.

⁴ Accuracy given as percent recovery of MS, unless otherwise indicated.

Table 7-2 Red Water Demonstration Tests Analytical Methods - Gas Samples

Analyte ¹	Analytical Method ²	Reference ³	Measurement Units	Minimum Detection Limit (MDL)	Precision (RPD) ⁴	Accuracy (% recovery) ⁵
Carbon monoxide	Method 10 continuous emission monitor (CEM)	BIF	ppmv	1	± 2% of span	± 5% of span
Carbon dioxide	Method 3	NSPS	%	0.5	± 0.5%	± 0.25% of span
Nitrogen oxide	Method 7E	NSPS	ppmv	1	± 3% of span	± 2% of span
Ammonia	P&CAM 20.5	MAS&A	ppmw	10	NR	NR
Oxygen	Method 3, or Method 3A	NSPS	%	0.25	± 0.5% ± 3% of span	± 0.25% of span ± 2% of span
Sulfur dioxide	Method 6C	NSPS	ppmv	1 ppmv	± 3% of span	± 2% of span
SVOCs	8270	SW-846	ug	100	< 35%	10-150
VOCs	8240	SW-846	ng	20	< 10	85-115

¹ Acronyms presented on Tables 5-2 and 6-2.

² P&CAM denotes Physical and Chemical Analytical Method.

³ BIF denotes methods presented in 40 CFR, Appendix B, "Federal Register," Volume 54 No. 206, October 1989, and the "Methods Manual for Compliance with BIF Regulations Burning Hazardous Waste in Boilers and Industrial Furnaces," USEPA, December 1990. NSPS denotes methods in "New Source Performance Standards," Test Methods and Procedures, 40 CFR 60, Appendix A. MAS&A denotes methods in Methods of Air Sampling and Analysis.

SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986.

⁴ Precision given as Relative Percent Difference of duplicate samples unless otherwise indicated.

⁵ Accuracy given as percent recovery of MS, unless otherwise indicated.

Table 7-2 (continued)

Analyte ¹	Analytical Method ²	Reference ³	Measurement Units	Minimum Detection Limit (MDL)	Precision (RPD) ⁴	Accuracy (% recovery) ⁵
Dioxins/furans	23	NSPS	pg	30	<35%	40-135%
	8290	SW-846				
	3510	SW-846				
	3560	SW-846				
Metals	3010/3050/6010 7470	SW-846 SW-846	ug/L	10	<60	65-130
HCl/Cl ₂ gas	9056	SW-846	ppmw	10	± 25% of range	85-115
Particulates	5	NSPS	mg/m ³	5	NR	NR

¹ Acronyms presented on Tables 5-2 and 6-2.

² P&CAM denotes Physical and Chemical Analytical Method.

³ BIF denotes methods presented in 40 CFR, Appendix B, "Federal Register," Volume 54 No. 206, October 1989, and the "Methods Manual for Compliance with BIF Regulations Burning Hazardous Waste in Boilers and Industrial Furnaces," USEPA, December 1990. NSPS denotes methods in "New Source Performance Standards," Test Methods and Procedures, 40 CFR 60, Appendix A. MAS&A denotes methods in Methods of Air Sampling and Analysis.

SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986.

⁴ Precision given as Relative Percent Difference of duplicate samples unless otherwise indicated.

⁵ Accuracy given as percent recovery of MS, unless otherwise indicated.

Table 7-3 Red Water Demonstration Tests Analytical Methods - Solid Samples

Analyte ¹	Analytical Method	Reference ²	Measurement Units	Minimum Detection Limit (MDL)	Precision (RPD) ³	Accuracy (% recovery) ⁴
SVOCs	8270	SW-846	ug/kg	10	< 30	70-130
VOCs	8240	SW-846	ug/kg	10	< 30	70-130
Metals	6010 200	SW-846 EPA	mg/kg	NSIM	< 35	80-120
Salts (inorganic)	7770/9056	SW-846	mg/kg	NSIM	NA	NA
Ignitability	1010/1020	SW-846	Flash Point > 140°F	NA	NA	NA
Corrosivity	9041/9042	SW-846	pH < 2 or pH > 12.5	NA	NA	NA
Reactivity	9030 (sulfide) 9010 (cyanide)	SW-846	mg/L mg/L	< 1 0.1	NSIM NSIM	NSIM NSIM

¹ Acronyms presented on Table 6-2; NSIM denotes not specified in method; NA denotes not applicable.

² SW-846 denotes methods listed in "Test Methods for Evaluating Solid Waste, Physical and Chemical Methods," SW-846, 3rd Edition, September 1986.

EPA denotes methods listed in "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, Revised March 1993.

³ Precision given as Relative Percent Difference of duplicate samples unless otherwise indicated.

⁴ Accuracy given as percent recovery of MS, unless otherwise indicated.

8.0 Sample Identification, Collection, Packaging, and Shipping

8.1 Sample Identification Procedures

Each sample will be assigned a unique alpha-numeric sample identification number. This will consist of:

- Project number
- Technology demonstration (WAO or CBC)
- Sample location identifier (identified in Tables 5-2 and 6-2)
- Test run number (identified in Tables 5-1 and 6-1).

Sampling events will be documented on logs or in project-specific log books.

8.2 Sample Collection Procedures

Samples will be collected at the times and locations specified in Sections 5 and 6 of this Test Plan. A sufficient quantity of sample must be collected to ensure that the analyses and all quality assurance/quality control (QA/QC) procedures can be properly conducted. Tables 8-1, 8-2, and 8-3 present the required sample containers, preservation methods, and maximum holding times for samples collected during the test program.

8.2.1 Liquid Sample Collection Procedures

Liquid samples will typically be grab samples of waste feed (red water) and treated effluent. Sample volumes, holding times, and preservative requirements are presented on Table 8-1.

Bioassay (acute and chronic toxicity) tests require special collection procedures presented in their respective test method and summarized below:

- Prepare effluent water by collecting four equal-volume grab samples every 15 minutes over a 1-hour time period composited into a single sample.
- The dilution water should be a representative of the receiving water, and should be obtained from a point as close as possible to, but upstream or outside of the zone influenced by the effluent. If acceptable dilution water cannot be obtained from the receiving stream, some other uncontaminated, well-aerated surface or ground water or commercially available test water may be used.

8.2.2 Gas Sample Collection Procedures

As indicated on Table 6-2, gas samples will typically be composite samples collected by collection trains. The collection systems to be used for the gas sampling include:

- Modified Method 5 - SW-846 Method 0010
- Multi-metal train - SW-846 Method 0012
- Volatile Organic Sampling Train (VOST) - SW-846 Method 0030
- Hydrochloric Gas Sampling Train - EPA Method 0050
- Point location - EPA Method 1
- Velocity, temperature and pressure - EPA Method 2
- Molecular weight (oxygen and carbon dioxide) - EPA Method 3
- Moisture - EPA Method 4
- Particulates - EPA Method 5.

The referenced collection method should be consulted for more information on gas sampling procedures. Sample volumes, holding times, and preservative requirements are presented on Table 8-2.

8.2.3 Solid Sample Collection Procedures

Solid samples will be grab and composite samples of ash produced by the CBC pilot-test unit. Sample volumes, holding times, and preservative requirements are presented on Table 8-3.

8.3 Sample Packaging and Shipping Procedures

The majority of the samples will be analyzed onsite by the host facility's laboratory; these samples may be placed in a sample cooler and hand-carried by a member of the project team and delivered to the host facility's laboratory.

Samples that will be analyzed offsite are expected to be able to be shipped as "not-restricted" based on the following assumptions:

- The samples do not meet the LD₅₀ limits of a DOT Class 6 Poison
- The samples do not meet the definition of miscellaneous dangerous goods (DOT Class 9 Materials) because they do not emit a noxious odor
- The samples are not a hazardous substance per 49 CFR Section 171.8
- The samples are not Federally regulated hazardous wastes because they are environmental samples for analysis.

The validity of these assumptions must be assessed upon receipt of red water characterization data.

Samples will be contained in the appropriate containers and preserved as indicated in Tables 8-1, 8-2, and 8-3. The sample containers will be packed with bubble pack or other protective material to avoid breakage. In addition, vermiculite will be placed in the sample shipment containers to absorb liquids should breakage occur. The sample containers and protective packaging will be placed in a sturdy, approved shipping container (e.g., plastic cooler) for shipment via an overnight delivery service. The outside of the shipping container will be labeled with the address of the shipper and the destination laboratory, and "This End Up:" and "Not Restricted" labels will be placed on the container.

Samples will be accompanied by a chain-of-custody form that records each sample and the names of individuals responsible for sample collection, shipment and receipt. A sample is considered in custody if it is:

- In a person's actual possession
- In view, after being in physical possession
- Locked so that no one can tamper with it, after having been in physical custody
- In a secured area, restricted to authorized personnel.

The chain-of-custody form typically is a two-part form consisting of a white original and a yellow field copy. The forms often are pre-printed with a unique six-digit chain-of-custody control number in the upper-right-hand corner. The white copy should always accompany the sample, and the yellow field copy should be retained in the field project file. The contents of this file are eventually transferred to the project central file at the completion of the field program or at intervals designated by the Project Manager.

The chain-of-custody form shall be signed by each individual who has the samples in his/her possession. The chain-of-custody record shall be prepared as follows:

- The person collecting samples shall initiate a field chain-of-custody record for each sample collected. Every sample shall be assigned a unique identification number that is entered on the chain-of-custody form. Samples can be grouped for shipment and use a common form.

- If the person collecting the samples does not transport the samples to the laboratory or deliver the sample containers for shipment, the first Relinquished By _____, Received By _____ shall be completed in the field. The names of all members of the sampling team shall be listed on the chain-of-custody form.
- The person transporting the samples to the laboratory or delivering them for shipment shall sign the Relinquished By _____.
- If the samples are shipped to the laboratory by commercial carrier, the original chain-of-custody/request for analysis form shall be sealed in a watertight container and placed in the shipping container, and the shipping container shall be sealed before it is given to the carrier.
- If the samples are directly transported to the laboratory, the original chain-of-custody form shall be kept by the person delivering the samples.
- For samples shipped by commercial carrier, the waybill shall serve as an extension of the chain-of-custody record between the final field custodian and receipt in the laboratory. (The carrier and waybill number will be written on the chain-of-custody/request-for-analysis form. If the original chain-of-custody form is sealed in the shipping container before the waybill number is received, then this number will be written on the copy of the chain-of-custody form).
- Upon receipt of the samples in the laboratory, the Quality Control Coordinator or representative shall open the shipping containers, compare the contents with the chain-of custody record, and sign and date the record. The Quality Control Coordinator will also record the carrier and waybill number on the original chain-of-custody form, if it is not already present. The Quality Control Coordinator will check the temperature, if appropriate, inside the shipping container and record the reading on the chain-of-custody form. Any discrepancies shall be noted on the chain-of-custody form.
- If discrepancies occur, the samples in question shall be segregated from normal sample storage and the field personnel immediately notified.
- The chain-of-custody form is completed after sample disposal.
- Chain-of-custody records shall be maintained with the records for a specific project, and become part of the data package.

A request-for-analysis should be completed by field personnel or other project personnel if appropriate. It is imperative that the request for analysis be provided so that the analytical requirements can be defined and sample holding times will not be exceeded.

Table 8-1
Sample Volume, Containers, Holding Times, and Preservatives - Water Samples

Analyte ¹	Volume Required (mL)	Sample Container ²	Maximum Holding Time	Preservation
pH	25	P, G	Analyze immediately	None required
COD	50	P, G	28 days	H ₂ SO ₄ to pH < 2
BOD	500	P, G	28 days	Cool to 4°C
TOC	100	P, G	28 days	H ₂ SO ₄ to pH < 2
TVS	100	P, G	7 days	Cool to 4°C
TS	100	P, G	7 days	Cool to 4°C
TDS	100	P, G	7 days	Cool to 4°C
TSS	500	P, G	7 days	Cool to 4°C
Chlorides	50	P, G	28 days	None required
Nitroaromatics	50	G	7 days	Cool to 4°C
2,4-DNT	50	G	7 days	Cool to 4°C
2,4,6-TNT	50	G	7 days	Cool to 4°C
Nitrite	50	P, G	2 days	Cool to 4°C
Nitrate	100	P, G	2 days	Cool to 4°C
Sulfate	50	P, G	28 days	Cool to 4°C
Acute toxicity	100	G	6 hours	Na ₂ S ₂ O ₃ , Cool to 4°C
Chronic toxicity	100	G	6 hours	Na ₂ S ₂ O ₃ , Cool to 4°C
Density	100	P, G	48 hours	Cool to 4°C
Heat content	50	P, G	NA	NA
Ash content	10 grams	P, G	None	None required
Total chlorine	200	P, G	Analyze immediately	None required
SVOCs	1000	G	7 days before extraction; 40 days after extraction	Cool to 4°C
Metals	500	P, G	6 months	HNO ₃ to pH < 2

¹ Acronyms presented on Tables 5-2 and 6-2; NA denotes not applicable.

² P denotes polyethylene; G denotes glass.

Table 8-2
Sample Volume, Containers, Holding Times, and Preservatives - Gas Samples

Analyte ¹	Volume Required	Sample Container	Maximum Holding Time	Preservation
Carbon monoxide ²	NA	NA	NA	NA
Carbon dioxide	1 L	mylar bag	4 hrs	NA
Nitrogen oxide ²	NA	NA	NA	NA
Ammonia	1 L	polyethylene jar	NA	NA
Oxygen	1 L	mylar bag	4 hrs	NA
Sulfur dioxide ²	NA	NA	NA	NA
SVOCs	1-3 m ³	XAD-2 resin tube	extraction - 7 days analysis - 40 days	Cool to 4°C
VOCs	20 L/sample	VOST resin tube	14 days	Cool to 4°C
Dioxins/furans	1-3 m ³	XAD-2 resin tube	extraction - 14 days analysis - 40 days	Cool to 4°C
Metals	1-2 m ³	Clear glass wide mouth jar	6 months (Cr ⁺⁶ 30 days)	Nitric acid, cool to 4°C
HCl/Cl ₂ gas	1-2 m ³	Glass container	30 days	Cool to 4°C
Particulates	1-2 m ³	Glass container and petri dish	30 days	Cool to 4°C

¹ Acronyms presented on Tables 5-2 and 6-2; NA denotes not applicable.

² Analysis by continuous monitor.

Table 8-3
Sample Volume, Containers, Holding Times, and Preservatives - Solid Samples

Analyte ¹	Amount Required	Sample Container ²	Maximum Holding Time	Preservation
SVOCs	30 grams	G	7 days before extraction; 40 days after extraction	Cool to 4°C
VOCs	5 grams	G	14 days	Cool to 4°C
Metals	25 grams	G	6 months	Cool to 4°C
Salts (inorganic)	200 grams	P, G	6 months	None required
Ignitability	200 grams	P, G	14 days	None required
Corrosivity	100 grams	P, G	Immediately	None required
Reactivity	40 grams	P, G	7 days	None required

¹ Acronyms presented on Table 6-2.

² P denotes polyethylene; G denotes glass.

9.0 References

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